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EVALUATION OF POLYPHENYLENE SULFIDE

PDO 6984844, Topical Report

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SUMMARY

Phillips Petroleum Company's R-4 polyphenylene sulfide (PPS) was evaluated. The chemical structure was verified, the polymer was characterized, and the physical characteristics were determined. A chemical evaluation determined the glass transition temperature to be 118°C and that decomposition begins at about 375°C.

(AUTHOR, MODIFIED)

A sixteen-line molding matrix was used to produce test specimens for a statistical analysis of the physical characteristics of the molding resin. Three molding variables--injection pressure, mold temperature, and melt temperature--each had five levels of variance while the mold fill time had three levels. All other molding conditions were held constant.

Polyphenylene sulfide can be molded successfully under a wide range of conditions. It has low shrink along with low differential shrink and warp characteristics, as well as a 260°C heat distortion temperature.

ABSTRACT

The results of this study indicate that PPS is a very strong, stable material having a high temperature resistance. It is solvent resistant and can be used where aromatic and chlorinated solvents are used. A drawback that would possibly influence its selection would be the opaque dark brown color, which also precludes it from being readily pigmented.

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SUMMARY

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DISCUSSION

SCOPE AND PURPOSE

Polyphenylene sulfide is a relatively new polymer. This material was selected for evaluation for advanced engineering applications because of its reported physical strength retention at temperatures up to 500°F (260°C). Physical and chemical properties of the material were determined, and its processability was evaluated. The information will assist in making accurate first-cut molds, provide knowledge about process limitations, and facilitate faster process tuning.

PRIOR WORK

Data were generated in PDO 6984565 "High Temperature Thermoplastics," which was concluded in January 1971, from an early development lot of Ryton. These data are compared in this report to the present production lot data.

ACTIVITY

Polyphenylene sulfide (PPS) Ryton R-4 containing 40 percent glass reinforcement, produced by Phillips Petroleum Company, was evaluated chemically and physically to provide better first-attempt molding of production parts.

Chemical Evaluation

Thermogravimetric analysis (TGA) indicates that PPS is very stable against oxidation. Its decomposition begins at 375°C in air and 395°C in nitrogen. The glass transition temperature, as determined by differential scanning calorimetry (DSC), was 118°C.

A solvent and extraction study was performed to determine the solubility of PPS in chloroform, toluene, acetone, ethanol, and n-hexane. The maximum solubility was 0.0078 percent after 46 hours in chloroform. A 7-day Soxhlet extraction in chloroform was analyzed and found to consist of unreacted starting chemicals and low molecular weight polymer.

The mass spectroscopic analysis of the extraction residue yielded the following information. From 180°C through 210°C the outgassing is mainly chlorophenoxy compounds such as PhCl,* ClPhO, C_7H_5ClO, $C_7H_5ClO_2$, $C_{12}H_{14}ClO$, and ClPhOPhOH. From 215°C through 240°C peaks for sulfur-containing fragments such as (Ph-S-PH)+ and (Ph-S-Ph-S-Ph)+ begin appearing with all of the chlorine fragments gone.

*Ph (phenyl)

From 255°C through 350°C there is steady increase in intensity of the phenylene sulfide fragments such as (Ph-S-Ph)+, (S-Ph-S-Ph-S)+, $(Ph_3-S_2)+$, $(Ph-S)_3+$ and $(Ph-S)_4+$.

This analysis indicates that the polymer structure is a pure polyphenylene sulfide. The elemental analysis agrees well with the theoretical values (Table 1).

Table 1. Elemental Analysis

Element	Composition (Percent)	
	Actual	Theoretical
Carbon	68.8	66.7
Hydrogen	3.9	3.7
Nitrogen	0	0
Sulfur	27.3	29.6

Physical Properties Analysis

This study consisted of a process limits study, the preparation and testing of physical test specimens, and an analysis of the data obtained.

Process Limits Study

The results of the process limits study were used to determine the range of conditions within which the polymer was capable of being molded. The manufacturer's recommended set points were used as a starting point and then the melt temperature, mold temperature, inject pressure, and inject speed were each varied to the high and low limits of polymer moldability.

Polyphenylene sulfide has a wide melt temperature range which is evidenced by the vendor's recommended melt temperature range of 575 to 675°F (302 to 357°C). However, about 600°F (316°C) was needed for consistent mold cavity filling. Temperatures of 610 to 690°F (321 to 366°C) were chosen as the melt temperature range for the study. Similar evaluations of the other molding variables established their effective ranges. Table 2 is a listing of the variables and their ranges used in the preparation of the test specimens for this study.

Table 2. Molding Study Variables

Injection (psi)	Pressure (MPa)	Mold Temperature (°F) (°C)	Melt Temperature (°F) (°C)	Fill Time Seconds
3000	(20.7)	150 (66)	610 (321)	--
4500	(30.1)	200 (93)	630 (332)	4 (A)
6000	(41.1)	250 (121)	650 (343)	2 (B)
7500	(51.8)	300 (149)	670 (354)	1 (C)
9000	(62.1)	350 (177)	690 (366)	--
Inject time, 36 seconds Press closed time, 76 seconds Clamp pressure, 250 tons (2.24 MN) Screw speed, 45 RPM (4.7 rad/s) Cushion, 1/8 to 1/4 inch (3 to 6 mm) Back pressure, minimum Mold release, none				

Test Specimen Preparation

The test specimens were molded simultaneously in a six-cavity mold (GenK 2590) using a Lester 250-ton (2.24 MN) injection molding press, with the following tests applied to them.

The 4-inch-diameter (102 mm), 0.125-inch-thick (3 mm), edge-gated disks were used for visual evaluation, shrink in parallel and perpendicular directions, thickness, runout in thickness, warp, dielectric strength, and dielectric constant tests.

The 9-inch (229 mm), end-gated, tensile test bars were used for tensile strength and ultimate elongation tests.

The 5- by 0.5- by 0.125-inch (128 by 12.7 by 3.2 mm), end-gated, bars were used for 1/8-inch (3 mm) Izod impact strength, flexural strength, and flexural modulus tests.

The 5- by 0.5- by 0.25-inch, (128 by 12.7 by 6.4 mm) bars were used for 1/4-inch (6 mm) Izod impact strength and heat distortion temperature tests.

Sixteen experimental lines (different sets of conditions) were molded to test the extreme combinations of the molding variables. Each line was molded at three fill times: slow (4 seconds), medium (2 seconds), and high (1 second), effectively giving a 48 line study as shown in Tables 3 and 4. (16 lines x 3 speeds = 48)

Table 3. Molding Matrix for Test Specimens

Line Number	Injection Pressure (psi) (MPa)	Mold Temperature (°F) (°C)	Melt Temperature (°F) (°C)
1	4500 (31.0)	200 (93)	630 (332)
2	7500 (51.8)	200 (93)	630 (332)
3	4500 (31.0)	300 (149)	630 (332)
4	7500 (51.8)	300 (149)	630 (332)
5	4500 (31.0)	200 (93)	670 (354)
6	7500 (51.8)	200 (93)	670 (354)
7	4500 (31.0)	300 (149)	670 (354)
8	7500 (51.8)	300 (149)	670 (354)
9	3000 (20.7)	250 (121)	650 (343)
10	9000 (62.1)	250 (121)	650 (343)
11	6000 (41.4)	150 (66)	650 (343)
12	6000 (41.4)	350 (177)	650 (343)
13	6000 (41.4)	250 (121)	610 (321)
14	6000 (41.4)	250 (121)	690 (366)
15	6000 (41.4)	250 (121)	650 (343)
16	6000 (41.4)	150 (66)	610 (321)

Specimen Testing

The tensile strength, ultimate elongation, Izod impact strength, warp, mold shrinkage, and appearance were determined for each of the 48 lines. The flexural strength, flexural modulus, plastic deformation temperature, dielectric strength, and dielectric constant were determined only on lines 13-C and 14-C which were the two lines with the extremes in melt temperature coupled with fast inject speed. These two lines were chosen because they should detect maximum material degradation.

The average tensile strength, ultimate elongation, and impact strength are shown in Table 4. Table 5 contains the data for the physical characteristics chosen to evaluate polymer degradation.

Data Analysis

Tensile Strength

The average tensile strength of all lines was 16,640 psi (114.7 MPa) with 19,000 psi (131.0 MPa) being the highest recorded value.

The mold temperature is the most significant variable, giving increased strength with decreased mold temperature. The tensile strength is increased with increased melt temperature, inject

Table 4. Physical Characteristics

Number	Average Tensile Strength (psi x 10^2)*	Average Ultimate Elongation (Percent)	Average Izod Impact Strength ft-lb/in. (J/m)**	
			1/8 Inch (3 mm)	1/4 Inch (6 mm)
1-A	177	1.1	1.27	1.57
1-B	163	1.0	1.30	1.52
1-C	171	1.2	1.19	1.48
2-A	170	1.1	1.22	1.62
2-B	159	1.1	1.30	1.74
2-C	176	1.2	1.05	1.47
3-A	165	1.1	1.28	1.48
3-B	150	0.9	1.22	1.54
3-C	154	1.0	1.22	1.76
4-A	152	0.9	1.16	1.48
4-B	157	1.0	1.29	1.62
4-C	161	1.0	1.19	1.55
5-A	169	1.1	1.27	1.74
5-B	187	1.2	1.40	1.53
5-C	183	1.1	1.41	1.56
6-A	189	1.2	1.58	1.67
6-B	186	1.1	1.38	1.60
6-C	189	1.2	1.33	1.75
7-A	163	0.9	1.24	1.66
7-B	159	0.9	1.14	1.44
7-C	163	0.9	1.18	1.58
8-A	162	0.9	1.39	1.78
8-B	170	1.0	1.35	1.56
8-C	168	1.0	1.31	1.51
9-A	162	0.9	1.30	1.63
9-B	165	1.0	1.28	1.41
9-C	164	1.1	1.22	1.44
10-A	170	1.0	1.36	1.65
10-B	165	0.9	1.38	1.68
10-C	175	1.1	1.38	1.67
11-A	175	1.1	1.36	1.65
11-B	174	1.1	1.42	1.66
11-C	174	1.1	1.37	1.63
12-A	147	0.8	1.34	1.69
12-B	145	0.8	1.27	1.64
12-C	160	0.9	1.07	1.56
13-A	153	0.9	1.27	1.53
13-B	157	1.0	1.22	1.40
13-C	161	1.0	0.93	1.67
14-A	155	0.8	1.42	1.61
14-B	167	0.8	1.43	1.64
14-C	175	1.0	1.06	1.56
15-A	160	0.9	1.50	1.59
15-B	166	1.0	1.34	1.86
15-C	169	1.0	1.04	1.57
16-A	171	1.0	1.31	1.59
16-B	172	1.1	1.38	1.62
16-C	170	1.1	1.36	1.66

*1 psi = 6.895 kPa
**1 ft-lb/in. = 53.4 J/m

Table 5. Properties Used to Evaluate Polymer Degradation

Properties	Line 13c	Line 14c
Flexural Strength (psi x 10^3) (GPa)	27.7 (191.0)	27.8 (191.7)
Flexural Modulus (psi x 10^6) (GPa)	2.05 (14.1)	1.92 (13.2)
Plastic Deformation Temperature (°F) (°C)	499 (259)	502 (261)
Dielectric Strength (V/M) (k^V/mm)	406 (16.0)	385 (15.2)
Dielectric Constant 60 Hz 1 Hz	3.83 3.82	3.86 3.86

pressure, and fast fill time. The interaction of inject pressure with melt temperature gives further strength when both are at high levels.

The highest strength is obtained with sufficient inject pressure for fast fill, with high melt temperature, and with relatively low mold temperature. This would also allow for a short molding cycle and a high production rate.

Ultimate Elongation

The mold temperature is again the most significant variable, both directly and through interaction with melt temperature. Increased elongation is obtained with decreased mold temperature; the increase is greater if the melt temperature is also high. There is a direct correlation between tensile strength and percent elongation. Those specimens with high tensile strength have greater elongation at failure.

The variation in elongation for individual specimens was from 0.7 to 1.2 percent with a mean of 0.98 percent. The low elongation is due to the high glass loading of the polymer.

Izod Impact Strength

The average Izod impact for the 1/8 (3 mm) specimens was 1.29 ft-lb/in. (68.9 J/M). For the 1/4 inch (6 mm) specimens, it was 1.60 ft-lb/in. (85.4 J/M). Different inject pressure,

mold temperature, and melt temperature settings had little effect upon the predictability of the impact strength.

Mold Shrinkage

The mold shrinkage was obtained by gaging the diameter of the 4.0-inch (102 mm) disk in two directions. Diameter (D_1) was gaged in the direction of material flow and D_2 was gaged perpendicular to the direction of flow. The diameter of the mold cavity is 4.023 inches (102.184 mm).

The average mold shrinkage was found to be anisotropic with 0.00079 inch/inch (mm/mm) for D_1 and 0.0015 inch/inch (mm/mm) for D_2. These values are comparable to other 40 percent glass-filled molding resins.

There were eight of the lines in which the shrinkage for D_2 was less than D_1. There were seven lines that had parts larger than the mold diameter indicating a negative shrinkage factor. These occurred at medium to high injection pressures coupled with medium melt temperatures and fast fill times. An equal mold shrinkage factor in both directions for one line was obtained by using medium injection pressure and melt temperature coupled with a high mold temperature and fast fill time.

Warp

Warp was estimated by placing two 4.0-inch (102 mm) discs from each line back to back (Figure 1) and measuring the gap, with the warp being equal to one-half this measurement.

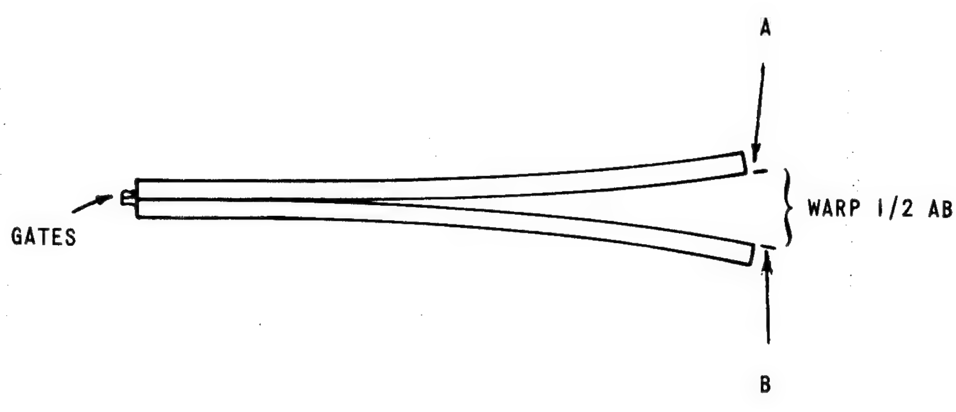

Figure 1. Illustration of Warp Determination

Typically warp is caused by a differential in mold shrinkage; however, this did not prove to be the case for PPS. The line mentioned that gave the same shrink factor for both directions also had the highest warp. The mold temperature is the most significant variable, both directly and through interaction with injection pressure or with fill time. A high mold temperature gives increased warp. Eleven of the thirteen lines having no warp were molded at the study midpoint mold temperature of 250°F or lower.

Thickness

The thickness of the 4.0-inch (102 mm) disc was gaged at five points: near the gate, at the center of the part, opposite the gate and at the two sides. The parts are all thicker near the gate because of packing and thinnest opposite the gate because of a lower cavity pressure. Thickness is directly related to injection pressure through interaction with increasing melt temperature. The maximum thickness was 0.127-inch (3.23 mm) the minimum was 0.123-inch (3.12 mm), with an overall mean thickness of 0.1248-inch (3.170 mm) for all specimens.

Flexural Strength and Flexural Modulus

The flexural strength and modulus were measured on test specimens from the two melt temperature extremes. There was no difference in the flexural strength at the melt temperature extremes. The flexural modulus is only slightly affected by the higher melt temperatures.

Heat Distortion Temperature

The melt temperature extremes had little effect on the heat distortion temperature. The average distortion temperature for a melt temperature of 610°F (321°C) was 499.3°F (259.6°C); for the 690°F (366°C) melt temperature, it was 502.0°F (261.1°C).

Electrical Properties

The dielectric strength and dielectric constant were determined on one sample each from the melt temperature extremes. The electrical properties should not be expected to change with processing variations.

Color and Surface Finish

No differences could be noted throughout the study because of the very dark brown color of the molding resin. There was a gold or tan color on the surface of some of the discs. This coloration was attributed to a non-glossy surface that was rich in glass, thereby allowing the glass to reflect the light through a very thin PPS coating.

Comparison of Development and Production Lots

The development lot of PPS that was evaluated on PDO 6984565 was compared to line 10-C from this production lot, because of the similarity of processing variables (Table 6).

The elemental analyses of the two lots are compared in Table 7.

These data correlate very well indicating that Phillips did not make any appreciable changes going into production with PPS. The only notable difference is the presence of oxygen in the development lot. Oxidation will result in the formation of sulfoxide groups which promote an increase in heat resistance; this possibly explains the higher heat distortion temperature for the development lot.

ACCOMPLISHMENTS

This 40 percent glass reinforced thermoplastic molding resin was evaluated and found to have very good physical characteristics, excellent chemical and solvent resistance, and resistance to temperatures up to 500°F (260°C).

Its physical strengths were found to be about equal to those of a 40 percent glass reinforced polycarbonate; however, it has superior chemical, solvent, and temperature resistance. The information gained from this study will allow a better understanding of PPS during molding and enable a realistic material specification to be written.

Table 6. Physical Characteristics of Development and Production Lots

Physical Characteristics	Development Lot	Production Lot
Tensile Strength, (psi)	18,900	17,500
(MPa)	(130.3)	(120.7)
Elongation, (Percent)	1.1	1.1
Izod Impact Strength		
1/8 inch (ft-lb/in.)	1.35	1.38
(J/M)	(72.0)	(73.7)
1/4 inch (ft-lb/in.)	1.53	1.67
(J/M)	(81.7)	(89.2)
Heat Distortion Temperature (°F)	515	502
(°C)	(268)	(261)
Mold Shrinkage,		
parallel to flow, in./in. (mm/mm)	0	0.0008
perpendicular to flow, in./in. (mm/mm)	0.0015	0.0015

Table 7. Elemental Analyses of Lots

Element	Composition (Percent)		
	Development Lot	Production Lot	Theoretical
Carbon	67.0	68.8	66.7
Hydrogen	3.7	3.9	3.7
Sulphur	27.3	27.3	29.6
Oxygen	1.9	0	0

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